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## XVI.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF  
CLARK UNIVERSITY, WORCESTER, MASS.

THE ACTION OF ACETOACETIC ETHER ON QUINONES:  
SYNTHESIS OF BENZOFURFURAN DERIVATIVES.

By M. IKUTA.

Presented by J. U. Nef, October 14, 1891.

WHEN chloranil is treated with sodium acetoacetic ether, one or two of its chlorine atoms can be replaced by acetoacetic ether groups. The study of the mono- and the di-substitution products obtained has led to an interesting synthesis of a number of furfuran derivatives.

*Trichlorquinoneacetoacetic Ether*,  $C_6Cl_3O_2(C_6H_5O_3)$ .

10 grams of acetoacetic ether, dissolved in about 100 c.cm. of benzine, are converted by means of sodium in the form of fine wire into the sodium salt. To the emulsion thus obtained is slowly added 18 grams (1 molecule) of finely powdered chloranil with continual shaking. The reaction sets in immediately, and the solution becomes colored blue, dark green, and finally brown. In order to complete the reaction the mass is either warmed on a water-bath or allowed to stand for several hours. The part insoluble in benzine, which is removed by filtration and repeatedly washed with fresh benzine, is a very bulky resinous mass, not practicable to work up further; it consists of sodium chloride, the sodium salts of the mono- and the di-substituted acetoacetic ether derivative of chloranil, besides much resinous matter.\*

The benzine from the clear orange-colored filtrate is then distilled

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\* From this portion, by acidifying and extracting with benzine and crystallizing from alcohol, a very slight amount of greenish yellow prisms melting at  $183^\circ$ , soluble in alkalis with blue coloration, and also dark brown needles insoluble in alkalis and melting above  $270^\circ$ , were obtained, but in too small quantity to admit of further study.

off, and the last traces of it removed by prolonged heating in an open dish on a water bath. A dark orange-colored oil is left, which is a mixture of acetoacetic ether, and the mono- and the di-substituted acetoacetic ether derivatives of chloranil. On adding a small amount of absolute alcohol, and stirring, the oil gradually solidifies to a crystalline mass. Recrystallized from alcohol, large orange rhombohedra of trichlorquinoneacetoacetic ether are obtained, as well as yellow rhombic crystals of dichlorquinonediacetoacetic ether, which two substances can readily be separated mechanically from one another; the latter is also somewhat less soluble in alcohol.

The red mono-substitution product was recrystallized from alcohol until it showed the constant melting point  $94^{\circ}$ , and then dried at  $70^{\circ}$  to  $75^{\circ}$  and analyzed.

0.3014 gram substance gave 0.4737 gram  $\text{CO}_2$  and 0.0738 gram  $\text{H}_2\text{O}$ .  
 0.2524 " " " 0.3158 "  $\text{AgCl}$  (Carius).

	Theory for $\text{C}_{12}\text{H}_9\text{Cl}_3\text{O}_5$ .	Found.
C	42.42	42.86
H	2.69	2.72
Cl	31.37	30.95

Trichlorquinoneacetoacetic ether is easily soluble in benzene, warm alcohol, and chloroform, moderately so in acetic acid, and difficultly soluble in ether. It dissolves in dilute alkalies and ammonia with blue color, changing quickly to orange-yellow on standing. An alcoholic solution of the substance gives a blood-red coloration with ferric chloride. With aniline it forms a colorless addition product melting at  $146^{\circ}$ , whereas fuming nitric acid changes it into a yellow very unstable substance. Reducing agents readily convert it into the corresponding hydroquinone.

*Trichlorhydroquinoneacetoacetic Ether,  $\text{C}_6\text{Cl}_3(\text{OH})_2(\text{C}_6\text{H}_3\text{O}_3)$ .*

The reduction of the quinone can be effected quantitatively by dissolving it in about 6 parts of alcohol, and adding alternately zinc dust and dilute sulphuric acid in small quantity until the solution becomes colorless. On adding water the hydroquinone separates out as an oil, which soon solidifies. Recrystallized from benzene, it is obtained in colorless rhombohedra, melting at  $132^{\circ}$ .

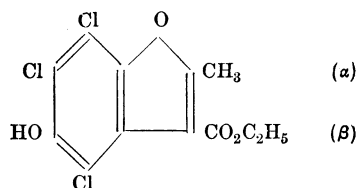
0.2204 gram substance dried at  $105^{\circ}$  gave 0.3444 gram  $\text{CO}_2$  and 0.0707 gram  $\text{H}_2\text{O}$ .

	Theory for $C_{12}H_{11}Cl_3O_5$ .	Found.
C	42.20	42.61
H	3.22	3.62

The hydroquinone is difficultly soluble in most organic solvents in the cold. It dissolves in alkalis with pale yellow color, changing quickly to dark green and yellow. An alcoholic solution gives with ferric chloride a blood-red coloration (*vide* the quinone).

The most noteworthy property of this substance is the ease with which it loses water going over into a benzofurfuran derivative.

*Trichlor p-oxybenzofurfuran  $\alpha$ -methyl  $\beta$ -carboxylic Ether,*



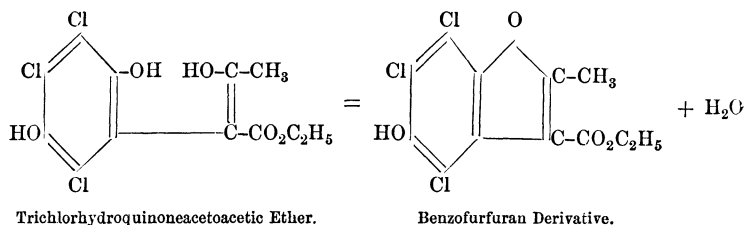
One part of trichlorhydroquinoneacetoacetic ether is dissolved in 10 parts of acetic acid, and, after adding a few drops of concentrated sulphuric acid, the solution is boiled for about an hour, or until on adding water to a portion a white precipitate is obtained which is not affected by ferric chloride. On adding a small amount of water to the hot acetic acid solution, the furfuran derivative crystallizes out in colorless transparent needles melting at  $138^\circ$ . The substance was recrystallized once from acetic acid, dried at  $110^\circ$ , and analyzed.

0.2530 gram substance gave 0.4131 gram  $\text{CO}_2$  and 0.0672 gram  $\text{H}_2\text{O}$ .  
 0.2005 " " " 0.2638 "  $\text{AgCl}$  (Carius).

	Theory for $C_{12}H_9Cl_3O_4$ .	Found.
C	44.51	44.53
H	2.71	2.95
Cl	32.92	32.54

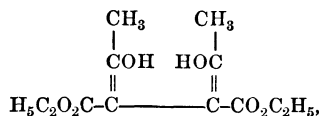
The substance is easily soluble in chloroform, less so in alcohol, ether, and cold acetic acid; it gives no coloration in alcoholic solution with ferric chloride, and dissolves in alkalis forming a colorless solution. On warming with concentrated sulphuric acid, a dark reddish blue coloration is obtained, which is very characteristic of the substance, as well as of all benzofurfuran derivatives. On heating with alcoholic potash, it is saponified to the corresponding monobasic acid.

The furfuran derivative is unquestionably formed according to the following equation:—

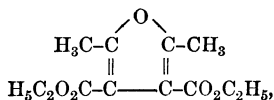


That acetoacetic ether is not a ketone, but a phenol-like body ( $\beta$ -oxy-crotonic ether), has been made highly probable by the work of Nef, soon to appear in Liebig's *Annalen*. In order, therefore, to explain the above reaction, the assumption of a pseudo or mobile modification of trichlorhydroquinoneacetoacetic ether is unnecessary; and the ease with which this anhydride formation takes place depends entirely on the position of the atoms in space.\*

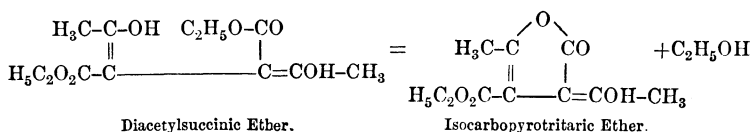
\* In some cases *only* the anhydride can be obtained (see *Ann. Chem. Liebig*). In this connection I would like to point out, that diacetylsuccinic ether,



according to Knorr, splits off on heating either water (200°), forming the furfuran derivative,

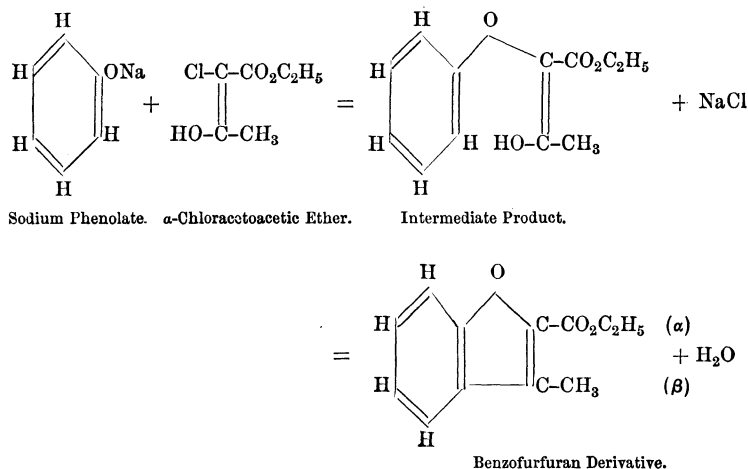


(Ber. d. chem. Ges., XVII. 2863), or alcohol (170°), forming isocarbopyrotritaric ether (Ber. d. chem. Ges., XXII. 159). Knorr thinks it probable that the latter substance is a ketopentamethylene derivative, just as Fittig (Ber. d. chem. Ges., XVIII. 3410) regards pyrotritaric ether as a ketopentamethylene derivative. It is however far more probable that the splitting off of alcohol from diacetylsuccinic ether takes place as follows:



Benzofurfuran derivatives were first obtained by Fittig and Ebert\* from cumarine derivatives, and later Rössing† obtained cumarone from *o*-aldehydophenoxyacetic acid.

A general method for obtaining such compounds has been published by Hantsch,‡ which consists in heating sodium salts of phenoles with  $\alpha$ -chloracetoacetic ether, e. g.:



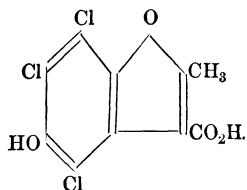
While the above method leads to  $\alpha$ -methyl  $\beta$ -carboxylic derivatives, that of Hantsch leads to  $\beta$ -methyl  $\alpha$ -carboxylic derivatives of benzofurfuran.

i. e. that under certain conditions of temperature the OH group of an acetyl radical is *nearer* in space to the  $\text{OC}_2\text{H}_5$  group of a  $\text{COOC}_2\text{H}_5$  group, whereas at a higher temperature ( $200^\circ$ ) the two OH groups of the acetyl radicals are *nearer* to one another in space, so that either alcohol or water is split off according to the temperature. Knorr also puts forward the above formula for isocarbopyrotritaric ether, but favors the ketopentamethylene formula because of the behavior of the ether towards alkalis (Ber. d. chem. Ges., XXII. 167). On the other hand, all the other reactions of isocarbopyrotritaric ether are best explained by the above lactone formula. It is therefore highly probable that a similar relationship exists in the very puzzling pyrotritaric acid series as has been shown by Feist (Liebig, Ann. Chem., CCLVII. 253) to exist in the case of dehydracetic acid. — J. U. Nef.

\* Ann. Chem. (Liebig), CCXVI. 170.

† Ber. d. chem. Ges., XVII. 3000.

‡ Ber. d. chem. Ges., XIX. 1292, 2930, XX. 1332.

*Trichlor p-oxybenzofurfuran  $\alpha$ -methyl  $\beta$ -carboxylic Acid,*

The ethyl ether just described is readily saponified by heating with twice the calculated amount of alcoholic potash on a water bath. After driving off the alcohol, and taking up with water, addition of dilute acetic acid precipitates the free acid in the form of colorless needles. It is purified by crystallization from glacial acetic acid, from which solvent it separates out into colorless transparent needles melting at  $258^{\circ}$  and subliming without change. The crystals become opaque on drying above  $100^{\circ}$ .

0.2736 gram substance dried at  $130^{\circ}$  gave 0.4090 gram  $\text{CO}_2$  and 0.0439 gram  $\text{H}_2\text{O}$ .

0.2130 gram substance dried at  $130^{\circ}$  gave 0.3076 gram  $\text{AgCl}$  (Carius).

	Theory for $\text{C}_{10}\text{H}_5\text{Cl}_3\text{O}_4$ .	Found.
C	40.61	40.76
H	1.70	1.78
Cl	36.04	35.72

In its behavior towards organic solvents, concentrated sulphuric acid, and alkalis, the free acid is like that of the ethyl ether.

*p-Dichlorquinonediaceoacetic Ether,  $\text{C}_6\text{Cl}_2\text{O}_2(\text{C}_6\text{H}_3\text{O}_3)_2$ .*

The method of preparing this substance is exactly the same as that described above for the mono-substitution product, except that twice as much sodium acetoacetic ether is taken. The crude product obtained is purified by crystallization from alcohol until the melting point of the substance reaches  $127-128^{\circ}$ . The alcoholic mother liquors always contain some mono-substitution product as well as greenish yellow prisms melting at  $183^{\circ}$  (mentioned in the foot-note, page 295). The substance is thus obtained in pure yellow rhombohedra or rhombic plates.

0.2492 gram substance dried at  $110^{\circ}$  gave 0.4515 gram  $\text{CO}_2$  and 0.0944 gram  $\text{H}_2\text{O}$ .

0.3003 gram substance dried at  $110^{\circ}$  gave 0.1947 gram  $\text{AgCl}$  (Carius).

	Theory for $C_{18}H_{18}O_8Cl_2$ .	Found.
C	49.88	49.41
H	4.16	4.21
Cl	16.39	16.04

The compound is easily soluble in benzine and chloroform, less so in alcohol, acetic acid, and ether. It dissolves in dilute alkalies, mild or caustic, forming deep bluish violet solutions, which soon change to brown. Sodid nitrite reacts on an alcoholic solution in the cold, forming a yellow substance which crystallizes in prisms, melts at  $184^\circ$ , and contains both chlorine and nitrogen. Fuming nitric acid converts the quinone into a very unstable yellow substance. An alcoholic solution is colored deep blood-red by addition of ferric chloride. One of the noteworthy properties is the ease with which the quinone forms addition products, and these are treated specially further on. A great many experiments were made in order to prove that the two acetoacetic ether groups are in the para position, but without success. This is, however, extremely probable, since in all cases yet known where two chlorine atoms in chloranil have been replaced the substitution takes place in para position (compare also Stieglitz, where two malonic ether groups are introduced in the para position \*).

*p-Dichlorhydroquinonediacetoacetic Ether*,  $C_6Cl_2(OH)_2(C_6H_3O_3)_2$ .

The above quinone is reduced to the hydroquinone in exactly the same way as described under trichlorhydroquinoneacetoacetic ether. The solid obtained by adding water to the alcoholic solution is purified by crystallization from benzine, from which solvent it separates out in colorless transparent rhombohedra, melting at  $154^\circ$ .

0.2114 gram substance dried at  $130^\circ$  gave 0.3816 gram  $CO_2$  and 0.0881 gram  $H_2O$ .

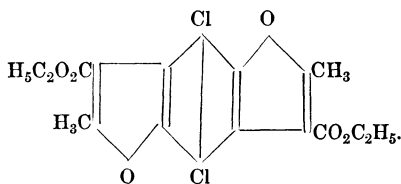
	Theory for $C_{18}H_{20}Cl_2O_8$ .	Found.
C	49.65	49.23
H	4.59	4.62

In its behavior towards ferric chloride, alkalies, and solvents, the hydroquinone is quite similar to trichlorhydroquinoneacetoacetic ether. The substance treated with dehydrating agents loses two molecules of water with ease, going over into a benzodifurfuran derivative.

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\* American Chem. Journal, XIII. 38.



*p*-Dichlorbenzo-*p*-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic Ether,

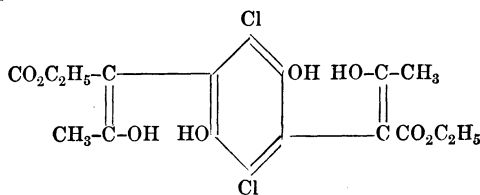
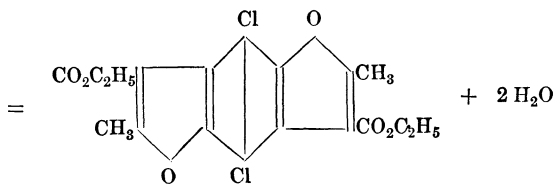
The above hydroquinone, when boiled for about an hour in acetic acid solution containing a few drops of concentrated sulphuric acid, is converted quantitatively into a benzodifurfuran derivative, which, since it is insoluble in alkalis, can easily be separated from the original substance. After precipitating by addition of water and treating with dilute sodic hydrate, the substance is crystallized from acetic acid (95%) and obtained in long transparent prisms melting at  $175^{\circ}$ .

0.2006 gram substance dried at  $120^{\circ}$  gave 0.3965 gram  $\text{CO}_2$  and 0.0748 gram  $\text{H}_2\text{O}$ .

0.2647 gram substance dried at  $120^{\circ}$  gave 0.1886 gram  $\text{AgCl}$  (Carius).

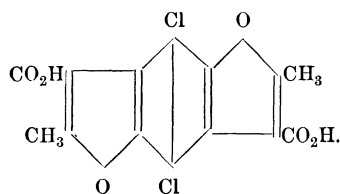
	Theory for $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{O}_6$ .	Found.
C	54.13	53.95
H	4.01	4.16
Cl	17.79	17.63

The furfuran compound is unquestionably formed according to the following equation:—

*p*-Dichlorhydroquinonediacetoacetic Ether.*p*-Dichlorbenzo-*p*-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic Ether.

The substance dissolved in concentrated sulphuric acid and warmed, gives a dark bluish green coloration which is very characteristic. It is difficultly soluble in most organic solvents except chloroform. By passing chlorine into a chloroform solution of the substance it forms a pale yellow oily addition product, which, on treating with zinc dust and acetic acid, is converted back to the original substance. Alcoholic potash saponifies it to the corresponding dibasic acid, —

*p-Dichlorbenzo-p-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic Acid,*



The ethyl ether described above is easily saponified by heating with twice the calculated amount of alcoholic potash. After driving off the alcohol, taking up with water, and acidifying with dilute acetic acid, the free acid separates out as a fine white powder, which, examined under the microscope, consists of crystalline needles. It sublimes at a higher temperature without melting, and is insoluble in organic solvents and water. It was therefore dissolved in potassic carbonate, precipitated by dilute acetic acid, and, after thorough washing with hot water, dried at 130° and analyzed.

0.2087 gram substance gave 0.3732 gram CO<sub>2</sub> and 0.0482 gram H<sub>2</sub>O.  
0.2461 “ “ “ 0.2013 “ AgCl (Carius).

	Theory for C <sub>14</sub> H <sub>8</sub> Cl <sub>2</sub> O <sub>6</sub> .	Found.
C	48.95	48.76
H	2.33	2.56
Cl	20.69	20.24

Concentrated sulphuric acid gives a bluish green coloration similar to that of the ether.

*The Addition Products of p-Dichlorquinonediacetoacetic Ether.*

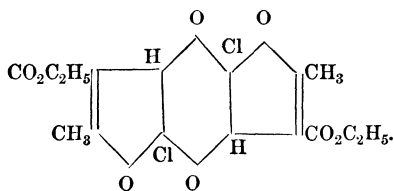
As above mentioned, this substance is characterized by the ease with which it forms addition products. Treated in chloroform solution with one molecule of bromine, a complete absorption of bromine takes place quickly without the slightest evolution of hydrobromic acid, and a colorless odorless substance separates out in heavy scales, which melt

at 216°. The analysis of the product, made at different times and washed with chloroform, gave no constant figures. The halogen determinations gave results varying from 1% to 5% too high for that calculated for a dibromide,  $C_{18}H_{18}Cl_2O_8$ ,  $Br_2$ , and this points to the presence of some tetrabromide. That the bromine has been added to the double bonds present in the quinone group and not to the acetoacetic ether residues follows: 1st, because the substance sublimes without decomposition; 2d, the corresponding dichlorhydroquinonediacetoacetic ether is acted upon only very slowly by bromine, and then with evolution of hydrobromic acid and formation of pungent derivatives affecting the eyes; 3d, the above addition product treated with zinc dust and acetic acid, or in alcoholic solution with zinc dust and dilute sulphuric acid, is converted chiefly into *p*-dichlorbenzo-*p*-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic ether.

The study of the product formed with bromine, though incomplete, is thus sufficient to show that it is an addition product, and its study, as well as that of other addition products, will be continued.

Noteworthy is the ease with which *p*-dichlorquinonediacetoacetic ether adds water, and is then converted into a new quinonefurfuran derivative.

*Quinone p-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic Ether Dihydrochloride,*



*p*-Dichlorquinonediacetoacetic ether is dissolved in 3 parts of acetic acid (95%) and warmed with a few drops of dilute sulphuric acid (1:5) on a water bath until the orange-colored solution becomes almost colorless. On diluting with water a pale yellow substance separates out in oily drops, which soon solidify to a white crystalline solid. The yield is almost quantitative, and after crystallizing from a mixture of chloroform and ether the substance was analyzed with the following result.

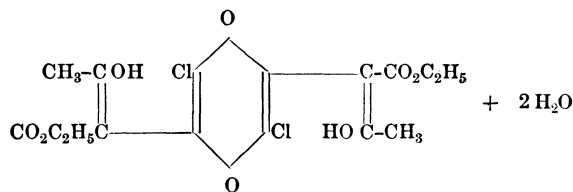
0.2010 gram substance dried in vacuum gave 0.3641 gram  $CO_2$  and 0.0746 gram  $H_2O$ .  
0.2112 gram substance dried in vacuum gave 0.1369 gr.  $AgCl$  (Carius).

	Theory for $C_{18}H_{18}Cl_2O_8$ .	Found.
C	49.88	49.40
H	4.15	4.12
Cl	16.39	16.03

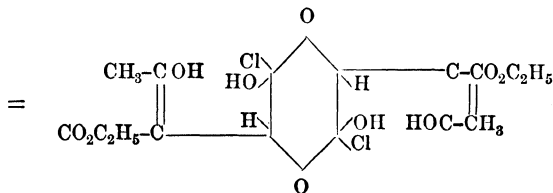
The substance melts at  $171^\circ$  to a pale yellow liquid, and sublimes without decomposition. It crystallizes in star-shaped leaflets or short prisms, and is easily soluble in organic solvents, but insoluble in water or mild alkalies. Warmed with concentrated sulphuric acid it gives a deep bluish green coloration, which is characteristic for furfuran derivatives.

Treated with twice the calculated amount of alcoholic potash, it is saponified to a dibasic acid,  $C_{14}H_{10}Cl_2O_8$ , which crystallizes from hot water in colorless needles. The acid is best purified by dissolving in soda and addition of dilute acids, when it separates out very slowly on standing. It decomposes with evolution of carbon dioxide on heating to  $220^\circ$ . An analysis gave results which agree closely with the formula  $C_{14}H_{10}Cl_2O_8$ , but show that the acid was not quite pure. (Found 43.53 % C, 2.96 % H, 20.50 % Cl. Theory, 44.56 % C, 2.65 % H, 18.95 % Cl.)

The formation of the above ester,  $C_{18}H_{18}Cl_2O_8$ , isomeric with *p*-dichlorquinonediacetoacetic ether is probably as follows. At first, an addition of two molecules of water takes place, just as has been observed in the case of many olefine derivatives :

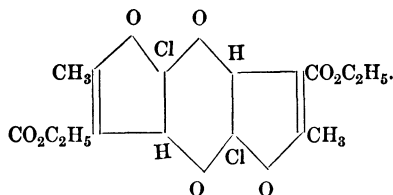


*p*-Dichlorquinonediacetoacetic Ether.



Addition Product.

The addition product formed then loses two molecules of water, going over into the furfuran derivative,



*Benzofurfuran Derivatives from Quinone and Acetoacetic Ether.*

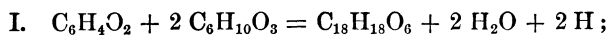
Von Pechmann\* describes a condensation product obtained from quinone and acetoacetic ether by means of alcoholic chloride of zinc. He gives it the formula  $C_{16}H_{16}O_6$ , and, as he states, it is formed according to the following equation:



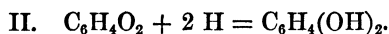
From the product  $C_{16}H_{16}O_6$ , he obtained further, by saponification with alcoholic potash, a dibasic acid,  $C_{14}H_{12}O_6$ .

Since v. Pechmann says that he does not intend to study the product obtained any further, I have taken up the investigation of these substances, especially since the behavior of the compound  $C_{16}H_{16}O_6$  is very similar to the benzofurfuran derivatives obtained from chloranil, and it therefore seemed probable that it possessed a similar constitution. The formulæ given by him for the above products are deduced from the mean result of a number of analyses. It is difficult, for instance, to see how from a *neutral* substance,  $C_{16}H_{16}O_6$ , by saponification, a *dibasic* acid,  $C_{14}H_{12}O_6$ , can be formed, since the former substance is not likely to contain methoxy groups. The study of these substances soon showed that the empirical formulæ given to the condensation product as well as the dibasic acid were incorrect.

The reaction between quinone and acetoacetic ether really takes place according to the following equation:



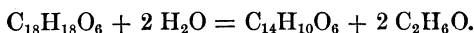
the two hydrogen atoms are used up in converting a molecule of quinone into hydroquinone:




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\* Ber. d. chem. Ges., XXI. 3005.

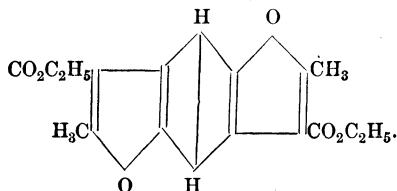
The condensation product thus has the formula  $C_{18}H_{18}O_6$ , instead of  $C_{16}H_{16}O_6$ ; by saponification with alcoholic potash two molecules of alcohol are split off, as follows :



The above mentioned dibasic acid has therefore the formula  $C_{14}H_{10}O_6$ , instead of  $C_{14}H_{12}O_6$ , and indeed the previous analyses agree better with this formula.

	Theory for $C_{14}H_{10}O_6$ .	For $C_{14}H_{12}O_6$ .	Von Pechmann's Analysis.
C	61.25	60.80	60.80
H	3.65	4.30	3.80

*Benzo-p-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic Ether,*



When quinone (one molecule) is heated in alcoholic solution with two molecules of acetoacetic ether in the presence of zinc chloride, the condensation product  $C_{18}H_{18}O_6$  is obtained, and as regards properties, etc., I can confirm in all detail the given statements. The alcoholic mother liquors contain, however, hydroquinone as well as a new substance,  $C_{12}H_{12}O_4$ , described below, which products have been overlooked. The analysis of the condensation product crystallized from acetic acid, gave figures agreeing well with the formula  $C_{18}H_{18}O_6$ . For the combustion it was carefully mixed with powdered chromate of lead, and the results obtained prove that it contains about 2% more carbon than found by v. Pechmann. The benzofurfuran derivatives all burn with great difficulty, so that most of the analyses given in this paper were carried out with lead chromate.

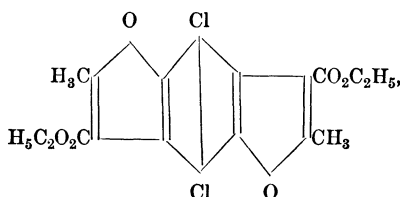
0.1942 gram substance dried at  $130^\circ$  gave 0.4625 gram  $CO_2$  and 0.0983 gram  $H_2O$ .

0.2027 gram substance dried at  $130^\circ$  gave 0.4840 gram  $CO_2$  and 0.1033 gram  $H_2O$ .

	Theory for $C_{18}H_{18}O_6$ .	Found.		Mean of former Analyses.	Theory for $C_{16}H_{16}O_6$ .
		I.	II.		
C	65.45	64.96	65.12	63.00	63.10
H	5.45	5.62	5.66	5.30	5.20

I give here, for convenience' sake, the properties of the substance.\* "Colorless needles, melting at  $184^{\circ}$ . Insoluble in water or alkalis, and soluble in chloroform and boiling acetic acid. The solution in concentrated sulphuric acid turns deep blue on warming. Bromine reacts, forming a crystalline derivative. Phenylhydrazin, benzoyl chloride, and hydriodic acid have no action on the substance."

The proof that the compound  $C_{18}H_{18}O_6$  has the constitution above given is as follows: chlorine converts it into a disubstitution product  $C_{18}H_{16}Cl_2O_6$ , which is identical with *p*-dichlorbenzo-*p*-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic ether,



already described and obtained from chloranil.

The substance is dissolved in acetic acid, and chlorine is passed into the solution for several hours in the sunlight, until a portion treated with zinc dust gives on addition of water a crystalline precipitate melting from  $155$ – $160^{\circ}$ , when the rest of the solution is treated in the same manner. By repeated crystallization from acetic acid (95%), the crude product was finally converted into a substance which melts constant at  $175^{\circ}$ , and crystallizes in long transparent needles identical in every respect with the *p*-dichlorbenzodifurfuran derivative  $C_{18}H_{16}Cl_2O_6$  described above. This was also confirmed by a halogen determination.

0.2138 gram substance dried at  $120^{\circ}$  gave 0.1499 gram AgCl (Carius).

	Theory for $C_{18}H_{16}Cl_2O_6$ .	Found.
Cl	17.79	17.35

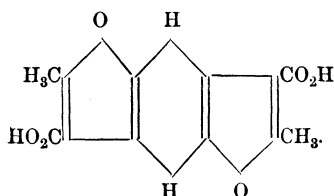
The substitution of the two hydrogen atoms of  $C_{18}H_{18}O_6$  is undoubtedly preceded by the formation of an addition product, just as  $C_{18}H_{16}Cl_2O_6$  gives, when treated with chlorine, an oily addition product as before mentioned, but the chlorine in these addition products is easily taken out by zinc dust and acetic acid.

These results prove conclusively the constitution of the condensation product  $C_{18}H_{18}O_6$ ; the constitution of the dibasic acid  $C_{14}H_{10}O_6$

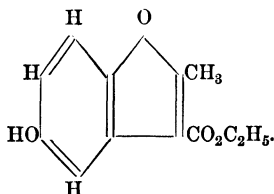
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\* Ber. d. chem. Ges., *loc. cit.*

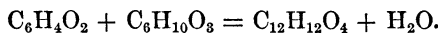
obtained from it by means of alcoholic potash necessarily follows; it is a benzo-*p*-difurfuran  $\alpha$ -dimethyl  $\beta$ -dicarboxylic acid,



*p*-Oxybenzofurfuran  $\alpha$ -dimethyl  $\beta$ -carboxylic Ether,



The above alcoholic chloride of zinc mother liquors, from which the product  $C_{18}H_{18}O_6$  has been removed, always contains hydroquinone and a furfuran derivative,  $C_{12}H_{12}O_4$ , besides acetoacetic ether. The hydroquinone was isolated, after driving off the alcohol, by taking up water and extracting the aqueous solution with ether. The condensation product  $C_{12}H_{12}O_4$  is obtained by allowing the alcoholic mother liquors to evaporate spontaneously, when it separates out in pearly scales. It is formed from quinone and acetoacetic ether according to the following equation:



The best yield (50% of quinone taken) is therefore obtained by heating quinone (1 molecule) with a molecule of acetoacetic ether in the presence of alcoholic zinc chloride. After filtering off the insoluble product  $C_{18}H_{18}O_6$ , which is invariably formed, the filtrate is allowed to evaporate in the air, and the pearly scales which separate out are brought on porous plates and washed with water. Recrystallized twice from petroleic ether (bpt. 70–80°), the substance is obtained in colorless scales or in flat needles, melting at 137°.

0.1889 gram substance dried at 110° gave 0.4510 gram  $CO_2$  and 0.0997 gram  $H_2O$ .

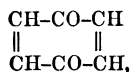


	Theory for $C_{12}H_{12}O_4$ .	Found.
C	65.45	65.12
H	5.45	5.86

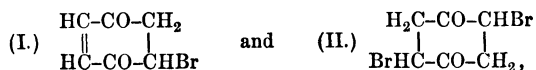
The benzofurfuran derivative is insoluble in water, but, since it contains a phenol group, soluble in alkalis. It is easily soluble in most organic solvents except petroleic ether. Warmed with concentrated sulphuric acid, it gives a reddish purple color.

The question now arises how the formation of the condensation products  $C_{18}H_{18}O_6$  and  $C_{12}H_{12}O_4$  can be explained. Sarauw \* has shown that, when quinone is treated with hydrobromic acid, hydroquinone and mono- and di-bromhydroquinone are found.

Since Nef † has unquestionably proved the presence of two double bonds in quinone,

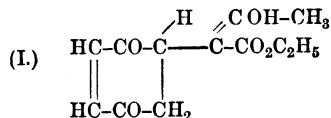


it is highly probable that the action of the hydrobromic acid is to form addition products,‡



and that these are then converted into monobrom- and *p*-dibromhydroquinone respectively, two of the hydrogen atoms in the addition product II. being removed by quinone, which goes over into hydroquinone.

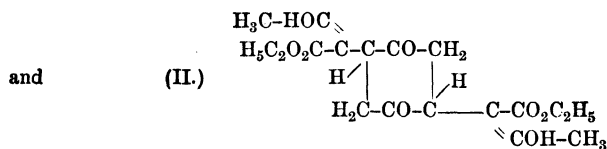
It is becoming more and more apparent that all the reactions shown by quinone which have hitherto not been understood are due to the ease with which such addition takes place; the activity of the double bonds in quinone has been further shown above by the addition of bromine and of water to *p*-dichlorquinonediacetoacetic ether. It is therefore very probable that acetoacetic ether reacts on quinone, just as hydrobromic acid, forming at first addition products:



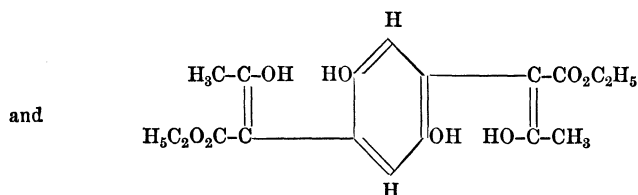
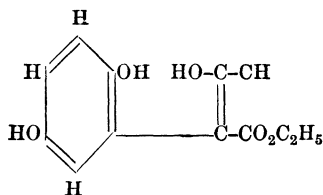
\* Ann. Chem. (Liebig), CCIX. 99.

† Amer. Chem. Journal, XII. 483, XIII. 422.

‡ Amer. Chem. Journal, XIII. 427.

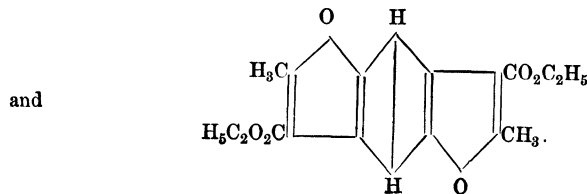
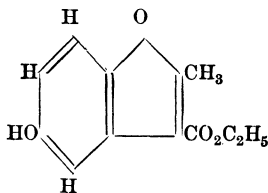


and that these are then converted into the hydroquinones,



(two of the hydrogen atoms in the addition product (II.) being taken up by quinone, forming hydroquinone).

The hydroquinones just as the corresponding hydroquinones obtained above from chloranil, then lose water under the influence of the dehydrating agent present, and go over into the benzofurfuran derivatives,



The above explanation becomes the more probable, because the addition of acetoacetic ether in the form of the sodium salt to olefine derivatives has already been accomplished in many cases by Michael,\* Auwers,† and others.

The work of which an account is given in this paper has been carried out under the direction of Prof. J. U. Nef, to whom I wish here to express my sincere thanks.

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\* J. prakt. Chem. (2), XXXV. 349, 449; Michael and Freer, Ibid., XLIII. 90.

† Ber. d. chem. Ges., XXIV. 307.

WORCESTER, MASS., September, 1891.